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(54) Title: FIBERS HAVING PHOSPHORUS-CONTAINING COATINGS

(57) Abstract

Mineral fibers are provided with a phosphorus-containing coating to impart high-temperature resistance without substantially affecting mechanical performance. Preferred mineral-fiber compositions according to the invention with relatively high levels of SiO_2 and low levels of Al_2O_3 and Fe_2O_3 compositions may advantageously be used for insulation. Such compositions have high-temperature resistance and high biosolubility, yet have properties which allow current processes to fabricate them into insulation. Preferably, the mineral fibers have a KI value ≥ 40.

FIBERS HAVING PHOSPHORUS-CONTAINING COATINGS

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of U.S. Patent Application Serial No. 08/566,530, filed December 4, 1995.

TECHNICAL FIELD AND INDUSTRIAL APPLICABILITY OF THE INVENTION

This invention relates to mineral fibers and their compositions. This invention further relates to phosphate-coated fibers. This invention also relates to high-temperature resistant mineral fibers which have high biosolubility.

BACKGROUND OF THE INVENTION

Mineral-fiber insulation is well known and has been a commercial product for a long period of time. The insulation is made from rock or slag fibers often referred to as mineral wool or rockwool. Fibrous mineral-wool insulation products generally comprise fibers bonded together by a cured thermoset polymeric binder to impart rigidity and improved mechanical performance to the insulation.

Mineral fibers have not been linked to disease in man. On the other hand, research has established that asbestos fibers when inhaled can cause significant disease in man. Though the exact mechanisms responsible for the biological activity of inhaled asbestos fibers is unknown, it is widely believed that their ability to remain in the lung for extended periods of time is an important factor. The durability or residence time in the lung of mineral fibers, however, appears to be much less than that of asbestos fibers.

Nonetheless, as an added precaution the German government has proposed regulations for mineral fibers. The proposed German regulations indicate that mineral wools should contain very high amounts of alkali and alkaline earth oxides to give the fibers a very high biosolubility. In particular, the proposed regulations set forth, as a criterion for sufficient biosolubility, a KI index where the sum of $CaO + MgO + Na_2O + K_2O + BaO + B_2O_3$ minus two times the Al_2O_3 must be at least 40 weight percent

	Amount (weight percent)			
Ingredient	Comp. A	Comp. B	Comp. C	Comp. D
SiO_2	44.82	39.67	40.89	51.35
Al_2O_3	8.96	9.99	7.23	2.50
MgO	10.90	13.31	13.72	11.90
CaO	33.49	37.03	38.17	33.10
Na_2O	0.04	--	--	0.50
K_2O	0.65	--	--	0.20
Fe_2O_3	0.09	--	--	0.30
TiO_2	0.49	--	--	0.15
MnO	0.56	--	--	--
P_2O_5	0.02	--	--	--

(The mean fiber diameters, in μm, for the fibers of compositions A, B, and C were 2.75, 2.11, and 2.13, respectively. As indicated, total iron is calculated in the above table as Fe_2O_3, which may be converted to an FeO basis by dividing by 1.1113.) An object of the invention is therefore to provide mineral fibers having high-temperature or fire resistance. A further object is to provide fibers with improved high-temperature performance without significant loss in mechanical performance. Another object of the invention is to develop fire-resistant fibers that also have high biosolubility.

We have found that the addition of high amounts of iron oxide improve the high-temperature or fire performance of fibers. The iron is substituted for an amount of SiO_2 to keep the solubility index at 40 weight percent. However, high amounts of iron further decrease the high-temperature viscosity and degrade the fiber-forming properties of the melt. Accordingly, an additional object of the invention is to achieve fire-resistant fibers that have desirable high-temperature viscosities and fiber-forming properties.

These and other objects have been achieved by phosphate- or phosphorus-coated fibers of the invention. The fibers have a composition as follows (in accordance with standard practice, certain ingredients or components are reported as oxides, with the

weight). Preferably, the combined amount of silica (SiO_2) and alumina (Al_2O_3) is at least 44 weight percent.

Preferred fiber compositions are as follows: 44 to 62 weight percent SiO_2, 0 to 8 weight percent Al_2O_3, 33 to 50 weight percent CaO + MgO, 0 to 5 weight percent $Na_2O + K_2O$, 0 to 6 weight percent total iron (present as Fe^{2+} or Fe^{3+}) expressed as FeO, and 0 to 1.2 weight percent total sulfur expressed as S^{2-}. Preferably, the combined amount of silica plus alumina is at least 48 weight percent.

More preferred fiber compositions are as follows: 47 to 59.5 weight percent SiO_2, 0 to 4 weight percent Al_2O_3, 36 to 48 weight percent CaO + MgO, 0 to 5 weight percent $Na_2O + K_2O$, 0 to 4 weight percent total iron (present as Fe^{2+} or Fe^{3+}) expressed as FeO, and 0 to 1 weight percent total sulfur expressed as S^{2-}. Preferably, the combined amount of silica and alumina is at least 51 weight percent.

Especially preferred fiber compositions are as follows: 51 to 59.5 weight percent SiO_2, 1 to 4 weight percent Al_2O_3, 36 to 45 weight percent CaO + MgO, 0 to 4 weight percent $Na_2O + K_2O$, 0 to 4 weight percent total iron (present as Fe^{2+} or Fe^{3+}) expressed as FeO, and 0 to 1.0 weight percent total sulfur expressed as S^{2-}. Preferably, the combined amount of silica and alumina is from 53 to 62 weight percent.

In a preferred embodiment of fiber compositions used in the invention, the ratio of the amount by weight of CaO to the amount by weight of MgO is from 1.5 to 6.

Exemplary fiber compositions that may be used in the invention include compositions A-D above. They also include commercial or known compositions E-I and composition J, which is a commercial rockwool used in high-temperature or fire-barrier applications, specified in the following chart:

under highly reducing conditions, the high-temperature performance improves. Further, the addition of a small amount of sulfide (e.g., 0.4 weight percent added as FeS) further improves the high-temperature performance. When such fibers were coated with $(NH_4)_2HPO_4$, the high-temperature performance was significantly improved. Notably, the fibers containing FeS, when coated with 3.6 weight percent $(NH_4)_2HPO_4$, performed as well in a simulated fire test as the standard mineral-wool composition J containing 5.4 % FeO. A linear shrinkage of 5 % was measured for the coated wool + FeS when heated to 930°C, compared to 6 % shrinkage for the standard composition.

Particularly preferred mineral-fiber compositions have a high SiO_2 content, low Al_2O_3 content, and low Fe_2O_3 content when compared to standard mineral-fiber compositions. Exemplary fiber compositions according to the invention are those consisting essentially of the following components in the specified amounts:

Ingredient	Amount (weight percent)
SiO_2	47.0 to 59.5
Al_2O_3	0 to 4.0
CaO + MgO	36.0 to 48.0
$Na_2O + K_2O$	0 to 5.0
FeO	0.1 to 4.0 (total iron, present as Fe^{2+} or Fe^{3+}, expressed as FeO)
S	0.05-1.0 (total sulfur expressed as S^{2-})

wherein $SiO_2 + Al_2O_3 \geq 51$ %, KI ≥ 40, and the portion of the iron present as Fe^{2+} is greater than 50% of total iron ($Fe^{2+}$and Fe^{3+}). Regarding the Fe^{2+}/Fe^{3+} ratio, Fe^{2+} is preferably greater than 50%, and may be as high as 80 %, or greater.

More preferred compositions meet the following specification:

invention by including sulfur in the composition and by melting the glass under reducing conditions. To determine the amount of sulfide necessary to produce bulk nucleations in the glasses, the procedures described at column 3 of U.S. Patent No. 4,366,251 may be followed.

Basically, one way of producing fibers contemplates two steps. First, silica, dolomite, clay, limestone, or other suitable raw materials are melted in a crucible, pot, or continuous glass-melting unit, depending on the quantity of product wanted and the manner of fiber formation to be utilized. Second, when a suitably homogeneous melt is attained, amorphous fibers are produced from the melt in any conventional manner, such as by drawing, spinning, or blowing.

Regarding the equipment for the production of mineral wool, one may use any known melting furnace for the production of traditional mineral wool. Either a cupola furnace or an electric furnace may be employed in combination with any known spinning device.

The melts can be produced in a cupola furnace in which is loaded a mixture of the raw materials. Also added is the required quantity of coke for causing burning and melting. If the melts are produced in an electric or gas-fired furnace, a reducing agent such as powdered carbon is added to chemically reduce the melt. The melt can be fiberized in a traditional spinning aggregate comprising four spinner wheels connected in a cascade.

Coating the mineral fibers with a phosphorus coating is preferably carried out by depositing a coat containing one or more phosphorus compounds on the surface of the fibers. When the fibers are heated, their linear thermal contraction at 930°C is preferably less than 20 percent. The amount of the phosphorus compound(s) coating the surface of fibers preferably falls in the range of from 0.5 to 10 % by weight, calculated as P_2O_5. The thermal contraction at 930°C is preferably less than 10% when the content of phosphorus compound is from 1 to 5 % by weight as P_2O_5.

Preferably, we adhere the phosphorus compound to the surface of the mineral fibers by spraying or other means of depositing a solution on the fibers. An alternative

the pyrophosphoric acid reacts with it to some extent and forms a high-temperature silicate-orthophosphate protective coating. This lessens attack and weakening of the fibers, while retaining improved high-temperature performance. Three exemplary additive combinations (i-iii) containing a phosphate and a colloidal silica are as follows:

	Parts (by weight)		
Additive ingredient	i	ii	iii
deionized water	185	178.3	182.5
MAP	5	5	5
Nyacol 9950	10	--	--
Nyacol DP5110	--	16.67	--
Nyacol 2040NH_4	--	--	12.5

The Nyacol additives are colloidal-silica products available from The PQ Corporation, with the Nyacol 9950 being provided as a 50% solution, Nyacol DP5110 being provided as a 30% solution, and Nyacol 2040NH_4 being provided as a 40% solution.

Also, two types of thermoset binders--phenolic resoles and polyacrylic acid based thermosets--work well in combination with the above additives. The ratio of thermoset binder to phosphate additive may vary from 90:10 to 40:60, respectively, with the preferred range being 75:25 to 50:50. Any suitable combination of thermoset binder and phosphate additive may be used.

Several polyacrylic acid based binders may be used in this invention in place of a phenolic resole. One example contains polyacrylic acid and a hydroxyl-functional crosslinking agent, e.g., "HF-5" resin available from Rohm & Haas.

The additive mixture should have an acidic pH, since too alkaline of a pH may cause the coated fiber to shrivel. The pH of the additive mixture may be appropriately adjusted, if necessary, using a suitable acidic agent, such as sulfuric acid.

The following examples illustrate preferred embodiments of the invention.

temperature falling in the range of from about 100°C to 125°C. In the fibers, the phosphorus compound was found to be contained in a concentration of 1.96 % by weight, computed as P_2O_5 The fibers were tested for thermal contraction. The results confirmed by the test that the fibers of the present invention showed only about 5.0% linear contraction when heated up to about 930°C.

Example 2

Whereas the fibers in Example 1 contained a relatively high amount of sulfur and were melted under reducing conditions to produce mostly FeO in the composition, the fibers of this example contained a very low amount of sulfur and were melted in a platinum crucible under oxidizing conditions (in an air atmosphere). Thus, additional nucleation of the fibers occurred in Example 1, while no additional bulk nucleation would have occurred in the present example described below.

In the pilot process used in this example, a fibrous mineral wool was formed from a molten stream that was fiberized by an air jet and collected as an assembly downstream in a static metal cage. The metal cage was completely enclosed by a larger metal box, and process air was continuously removed at the far downstream end of this enclosure by a flexible duct connected to an electric exhaust blower, preceded by an air filter to remove suspended droplets of binder. Binder was sprayed onto the fibers as an aqueous solution or dispersion using a binder ring containing spray nozzles. Application of the binder occurred immediately after the fiberizing or attenuation zone, and before the fibers entered the metal-collection enclosure.

In particular, binder was applied in the form of an aqueous spray using nozzles attached to a circular binder ring. The binder ring, the number of nozzles, and the spray pattern of the nozzles were selected to give a theoretical coverage of at least 100% of the fiber veil. The veil measured approximately 8 inches in diameter. A 21-inch i.d. (inside diameter), air-atomized binder ring with 20 tip openings was found to be suitable, and only 10 of the 20 ring tips were used (every other one was plugged). An SU12 air-atomized pressure spray setup (2850 fluid cap + 73160 air cap), available from Air Spray Systems, was chosen to provide a good spray pattern at a binder flow

Ex.	Fiber comp.	Binder	Phos.	Flowrate (gpm)	Total add. solids (%)	Inorg. solids (% total)	Avg. LOI (%)	Avg. P_2O_5 (%)
2a	K	Phen.	DAP	1.0	5.5	50	8.6	
2b	K	Phen.	DAP	0.5	11.0	50	15.4	4.75
2c	K	Phen.	DAP	0.5	7.7	50	7.3	
2d	K	Phen.	DAP	0.5	5.5	50	8.7	2.20
2e	K	Phen.	DAP	0.5	3.3	50	3.2	0.82
2f	K	Phen.	DAP	0.5	5.5	25	5.5	
2g	K	Phen.	DAP	0.5	5.5	25	6.8	
2h	K	Non.	MAP	0.5	5.5	40	9.0	
2i	K	Non.	SPyP	0.5	5.5	40	6.2	
2j	K	Non.	MAP/ silica	0.5	5.5	34/16	5.7	
2k	K	Non.	DAP	0.5	5.5	40	5.0	
II	K	Phen.	--	0.5	3.8	0	9.0	

As indicated in the above table, composition K, which has been identified previously, was used for the fibers in all examples. A phenolic ("Phen.") or non-phenolic ("Non.") binder was also employed in the examples--specifically, sodium-catalyzed RE-176 (available from Owens Corning, Newark, Ohio) was used in the additives of examples 2a-2g and II, and HF-5 resin (available from Rohm & Haas) was used in examples 2h-2k. The phosphate ("Phos.") employed in the additive ("add.") for each of examples 2a-2i was DAP ($(NH_4)_2HPO_4$), MAP ($NH_4H_2PO_4$), or SPyP ($Na_4P_2O_7 \cdot 10H_2O$). Colloidal silica, specifically, DP5110 (available from The PQ Corporation), was also added in example 2j. In examples 2a-2g and II the pH of the additive was adjusted to be acidic (pH = 5 to 6) using sulfuric acid. The total amount of additive present as solids, given in weight percent based on the weight of the fiber, is provided for each example along with the percentage of that total attributable to inorganic solids

departing from the spirit of the invention. Thus, the invention is intended not to be limited by the foregoing detailed description, but to be defined by the following claims and their equivalents.

wherein the amount of $SiO_2 + Al_2O_3 \geq 51$ weight percent, the amount of MgO ranges from 4 to 32 weight percent, the amount of CaO ranges from 15 to 43 weight percent, $KI \geq 40$, and greater than 50% of the total iron is present as Fe^{2+}; and

a coating on the mineral fiber, the coating including a phosphorus compound in an amount ranging from 0.5 to 10.0 weight percent calculated as P_2O_5 based on the total weight of the fiber plus the coating.

3. A mineral-fiber product according to claim 1 where the mineral fiber has the following composition:

Ingredient	Weight Percent
SiO_2	49.0 to 58.0
Al_2O_3	0.2 to 3.0
CaO + MgO	40.0 to 46.0
$Na_2O + K_2O$	0 to 3.0
FeO	0.1 to 3.0 (total iron expressed as FeO)
S	0.1 to 0.5 (total sulfur expressed as S^{2-})

wherein the amount of $SiO_2 + Al_2O_3 \geq 51$ weight percent, the amount of MgO ranges from 5 to 25 weight percent, the amount of CaO ranges from 15 to 41 weight percent, $KI \geq 40$, and greater than 50% of the total iron is present as Fe^{2+}.

4. A mineral-fiber product according to claim 1 where the mineral fiber has the following composition:

Ingredient	Weight Percent
SiO_2	51.0
Al_2O_3	2.5
CaO	32.9
MgO	11.8
Na_2O	0.5
K_2O	0.2

10. A mineral-fiber product as defined in claim 7, wherein said phosphorus compound is a phosphate of the formula MH_2PO_4, M_2HPO_4, $MHPO_4$, or M_3PO_4, where M is an alkali metal, alkaline earth metal, or ammonium.

11. A mineral-fiber product as defined in claim 7, wherein said phosphorus compound is $(NH_4)_2HPO_4$.

12. A mineral-fiber product as defined in claim 7, wherein said phosphorus content is from 1.0 to 5.0 weight percent.

13. A mineral-fiber product as defined in claim 7, wherein the sum of the weight percentages of any Na_2O, K_2O, CaO, MgO, BaO, and B_2O_3 minus two times the weight percentage of Al_2O_3 in the fiber composition is greater than or equal to 40.

14. A mineral-fiber product as defined in claim 7, wherein greater than half of the amount of iron is present as Fe^{2+}.

15. A mineral-fiber product as defined in claim 14, wherein the amount of SiO_2 is from 48.0 to 59.0 weight percent, the amount of Al_2O_3 is from 0 to 3.0 weight percent, the total amount of CaO and MgO is from 37.0 to 47.0 weight percent with the amount of MgO being from 4 to 32 weight percent and the amount of CaO being from 15 to 43 weight percent, the total amount of Na_2O and K_2O is from 0 to 4.0 weight percent, the amount of iron is from 0.1 to 3.0 weight percent expressed as FeO, the amount of sulfur is from 0.05 to 0.8 weight percent expressed as S^{2-}, and the sum of the weight percentages of any Na_2O, K_2O, CaO, MgO, BaO, and B_2O_3 minus two times the weight percentage of Al_2O_3 is greater than or equal to 40.

16. A mineral-fiber product according to claim 15, wherein the amount of

20. A mineral-fiber product as defined in claim 19, wherein said binder is a phenolic binder.

21. A mineral-fiber product as defined in claim 18, wherein said phosphorus compound is a phosphate of the formula MH_2PO_4, M_2HPO_4, $MHPO_4$, or M_3PO_4, where M is an alkali metal, alkaline earth metal, or ammonium.

22. A mineral-fiber product as defined in claim 18, wherein said phosphorus compound is $(NH_4)_2HPO_4$.

23. A mineral-fiber product as defined in claim 18, wherein said phosphorus content is from 1.0 to 5.0 weight percent.

24. A mineral-fiber product comprising:

a mineral fiber having a composition comprising 37 to 64 weight percent SiO_2, 0 to 12 weight percent Al_2O_3, 30 to 51 weight percent CaO + MgO, and 0 to 6 weight percent $Na_2O + K_2O$; and

a coating on the fiber comprising a phosphorus-containing additive in an amount providing a phosphorus content of from 0.5 to 10.0 weight percent calculated as P_2O_5 based on the total weight of the fiber plus coating.

25. A mineral-fiber product according to claim 24, wherein the composition of the mineral fiber further comprises 0 to 7.0 weight percent total iron (present as Fe^{2+} or Fe^{3+}) expressed as FeO, and 0 to 1.5 weight percent total sulfur expressed as S^{2-}.

26. A mineral-fiber product according to claim 24, wherein the phosphorus-containing additive is selected from the group consisting of: aluminum phosphate; diammonium hydrogen phosphate; monoammonium dihydrogen phosphate; phosphoric acid; sodium pyrophosphate; and calcium phosphate, dibasic.

27. A mineral-fiber product according to claim 25, wherein the coating further comprises a thermosetting binder.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/19326

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C03C 13/02, 13/06; D02G 3/00
US CL :501/36, 38; 428/378
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/36, 38; 428/378

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,332,699 A (OLDS ET AL) 26 JULY 1994 (26/07/94), see column 3, lines 5-35.	1-30
Y	US 4,194,914 A (MORIYA ET AL) 25 March 1980 (25/03/80) See column 2, lines 25-46.	1-30
A	US 4,381,347 A (CARBOL) 26 April 1983 (26/04/83) See entire document.	1-30
A	US 4,560,606 A (RAPP ET AL) 24 December 1985 (24/12/85) See entire document.	1-30
A	US 5,312,806 A (MORGENSEN) 17 May 1994 (17/05/94), See entire document.	1-30
A	US 5,250,488 A (THELOHAN ET AL) 05 October 1993 (05/10/93), See entire document.	1-30

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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